ATTRITION RESISTANT IRON-BASED CATALYST FOR F-T SBCRS

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ABSTRACT

The Fischer-Tropsch (F-T) reaction provides a way of converting coal-derived synthesis gas (CO+ H₂ to liquid fuels. Since the reaction is highly exothermic, one of the major problems in control of the reaction is heat removal. Recent work has shown that the use of slurry bubble column reactors (SBCRs) can largely solve this problem. The use of iron-based catalysts is attractive not only due to their low cost and ready availability, but also due to their high water-gas shift activity which makes it possible to use these catalysts with low H₂/CO ratios. However, a serious problem with the use of Fe catalysts in a SBCR is their tendency to undergo attrition. This can cause fouling/plugging of downstream filters and equipment; makes the separation of catalyst from the oil/wax product very difficult, if not impossible; and results in a steady loss of catalyst from the reactor.

Under a previous Department of Energy (DOE)/University Research Grant (UCR) grant, we have reported, for the first time, the development of demonstrably attrition-resistant Fe FTS catalysts having good activity, selectivity, and attrition resistance. These catalysts were prepared by spray drying Fe catalysts with potassium (K), copper (Cu), and silica (SiO₂) as promoters. SiO₂ was also used as a binder for spray drying. These catalysts were tested for activity and selectivity in a lab-scale fixed-bed reactor. Fundamental understanding of attrition is being addressed by incorporating suitable binders into the catalyst recipe. This has resulted in the preparation of a spray dried HPR-43 catalyst having aps of 70 μ m with high attrition resistance. This HPR-43 attrition resistant, active and selective catalyst gave 95% CO conversion through 125 hours of testing in a fixed-bed at 270°C, 1.48 MPa, H₂/CO=0.67 and 2.0 NL/g-cat/h with C₅⁺ selectivity of >78% and methane selectivity of less than 5% at an α of 0.9.

Research is proposed to enable further development and optimization of these catalysts by (1) better understanding the role and interrelationship of various catalyst composition and preparation parameters on attrition resistance, activity and selectivity of these catalyst (2) the presence of sulfide ions on a

precipitated iron catalysts and (3) the effect of water on sulfided iron FT catalysts for its activity, selectivity and attrition. Catalyst preparations will be based on spray drying. The research will employ, among other measurements, attrition testing and F-T synthesis at high pressure. Catalyst activity and selectivity will be evaluated using a small fixed-bed reactor and a continuous stirred tank reactor. Efforts during this reporting period have been devoted to catalyst attrition study and CSTR fabrication for reaction studies. The CSTR fabrication is completed. Reactions of some of the catalysts synthesized in our laboratory are scheduled to start this summer.

PUBLICATIONS AND PRESENTATIONS

- ▶ Bukur, D. B., Ma, W. P., Carreto-Vazquez, V., Nowicki, L. and Adeyiga, A. A., "Attrition Resistance and Catalytic Performance of Spray-Dried Iron Fischer Tropsch Catalysts in a Stirred Tank Slurry Reactor" Ind. Eng. Chem. Res., 43, 1359-1365,2004.
- ▼ Kandis Sudsakorn, James G. Goodwin, Jr., and Adeyinka A. Adeyiga, "Effect of Activation Method on Fe FTS Catalysts: Investigation at the Site Level Using SSITKA". Submitted, <u>Journal of Catalysis</u>, 2002.
- ▼ Adeyinka Adeyiga, Liang Hu, Efat Miamee, "Attrition-Resistant Iron-Based Catalyst for F-T SBCRS". Presentation, University Coal Research/Historically Black Colleges and Universities and Other Minority Institutions Programs Review Meeting, Pittsburgh, PA, June 4-5, 2002.
- Adeyinka Adeyiga, Liang Hu, Efat Miamee, "Development of Attrition-Resistant Iron-Based Catalyst for F-T Catalysts". Presentation, University Coal Research/Historically Black Colleges and Universities and Other Minority Institutions Programs Review Meeting, Pittsburgh, PA, June 4-5, 2002.
- ➤ Kandis Sudsakorn, James G. Goodwin, Jr., K. Jothimurugesan, and Adeyinka A. Adeyiga, "Preparation of Attrition Resistant Spray-Dried Fe Fischer-Tropsch Catalysts using Precipitated SiO2". Industrial and Engineering Chemistry Research, 2001, 40, 4778
- ✓ Adeyinka A. Adeyiga, "Development of Attrition-Resistant Iron-Based Fischer-Tropsch Catalysts". UCR-HBCU Contractors Review Conference, Pittsburgh, PA, June 4 6, 2001.

FACULTY, STAFF, AND STUDENT SUPPORT FOR THE PROJECT

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- [2] Zhao, R.; Goodwin, J.G., Jr.; Jothimurugesan, K.; Spivey, J.J.; Gangwal, S.K. Spray-dried iron Fischer-Tropsch catalysts. 1. Effect of structure on the attrition resistance of the catalysts in the calcined state. *Ind. Eng. Chem. Res.* **2001**, *40*, 1065.
- [3] Zhao, R.; Sudsakorn, K.; Goodwin, J.G., Jr.; Jothimurugesan, K.; Gangwal, S.K.; Spivey, J.J., Attrition Resistance of Spray-dried Iron F-T Catalysts: Effect of Activation Conditions. *Catal. Today*, in press **2001**.